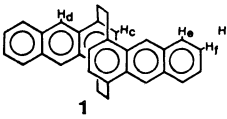
Layered Compounds. LII.[1] Syntheses of Eleven Anthracenophanes

Akio Iwama, Toshihiro Toyoda, Misaku Yoshida, Tetsuo Otsubo,
Yoshiteru Sakata, and Soichi Misumi*
The Institute of Scientific and Industrial Research, Osaka University, Suita, Osaka 565

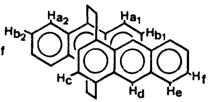
(Received February 20, 1978)

A series of layered cyclophanes where an anthracene ring is stacked in different modes with the same or other π-systems has been synthesized by the Hofmann elimination method or photodesulfurization for studying the transannular π-electronic interaction. Photochemical and thermal interconversions have been observed between *syn*-(1,4)anthracenophane and its isomer and have been discussed with reference to the X-ray crystal data. From the electronic spectra it has been established that the transannular interaction increases with overlapping between the two faced aromatic rings and that when the overlap between the two chromophores is the same, the interaction increases relative to the dimension of the faced chromophore.

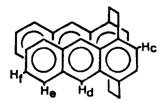
Recently a wide variety of [2.2]phanes containing benzene or heteroaromatic rings has been synthesized in order to study the effect of transannular π-electronic interactions on their physical and chemical properties.[2] If one or two benzene rings are replaced by naphthalene or anthracene rings, which have a larger molecular surface and lower ionization potential than benzene, it is expected that such cyclophanes will show stronger transannular interactions. Various types of [2.2]naphthalenophanes[3] have been prepared for this purpose, but [2.2]anthracenophanes other than [2.2](9,10)-anthracenophane[4] have not been studied. Since the anthracene ring has a lower symmetry and more bridging points than the benzene ring, some isomeric anthracenophanes differing in stacking mode between the two chromophores are feasible. These isomers appear to be good models for studying the effect of the magnitude and/or the mode of overlapping between anthracene and other π-systems upon transannular π-electronic interaction. A series of anthracenophanes has been prepared along this line, *i.e.*, three isomers of both [2.2]anthracenophane (**1**—**3**) and [2.2]naphthalenoanthracenophane (**4**—**6**) and two isomers of both [2.2]paracycloanthracenophane (**7**, **8**) and its dimethyl derivative (**9**, **10**). In addition, a triple-layered anthracenophane **11** has also been synthesized.



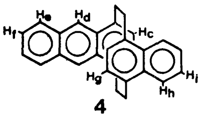
1



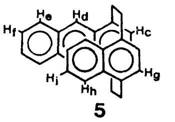
2



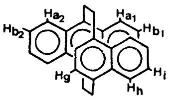
3



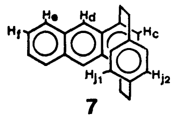
4



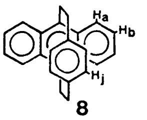
5



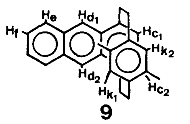
6



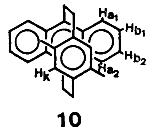
7



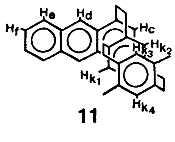
8



9



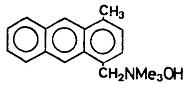
10



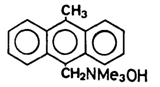
11

Results and Discussion

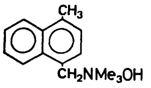
Syntheses. A quaternary ammonium salt **12** was prepared from 4-methylanthracene-1-carboxylic acid **17** as shown in Scheme 2. The other quaternary ammonium hydroxides **13**—**16** were obtained according to methods previously reported.[3c,3g,5] The syntheses of all the new cyclophanes **1**—**11** except for **9** and **10** were conducted as shown in Scheme 1 by the pyrolysis of the corresponding ammonium hydroxide or an equimolar mixture of two different bases in boiling xylene in the presence of a catalytic amount of phenothiazine. Yields of cyclophanes were relatively low as expected for the 1,6-Hofmann elimination. The synthesis of **9** and **10** was carried out by the coupling of 9,10- or 1,4-bis(halomethyl)anthracene with 2,5-bis(mercaptomethyl)-*p*-xylene,[6] followed by photodesulfurization in triethyl phosphite.



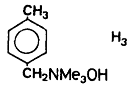
12



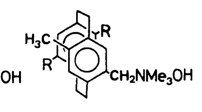
13



14



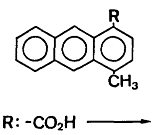
15



16 a: R=H
b: R=CH_3

12 → 1 + 3
12 + 13 → 2
12 + 14 → 4 + 5
13 + 14 → 6
12 + 15 → 7
13 + 15 → 8
12 + 16_b → 11
13 + 16 → 23

Scheme 1.

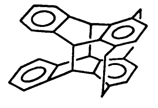


R: $-CO_2H \longrightarrow -CO_2Et \longrightarrow -CH_2OH$
17 18 19

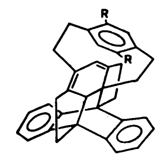
$\longrightarrow -CH_2Br \longrightarrow -CH_2NMe_3Br \longrightarrow$ 12
20 21

Scheme 2.

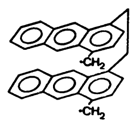
Separation and purification of the cyclophanes were achieved by careful column chromatography on silica gel and/or alumina followed by recrystallization. In the preparation of [2.2](1,4)anthracenophane and [2](1,4)naphthaleno[2](1,4)anthracenophane, both the *anti*- and *syn*-isomers, *i.e.*, **1** and **3**, and **4** and **5**, were isolated. The isomers are thermally stable and no interconversion between them was observed at room temperature. The structure of these isomers could be easily assigned by NMR analysis as described below. Pyrolysis of mixed ammonium bases, **13** and **15**, produced paracycloanthracenophane **8**. This was, however, not isolated in the reaction starting from [2.2]paracyclophane,[3c] probably due to an intramolecular Diels-Alder reaction as described below. Such instability of paracyclo(9,10)anthracenophane was observed in the attempted synthesis of the triple-layered (9,10)anthracenophane which is isomeric with **11**. Thus, the cross breeding reaction of **13** and **16** gave an unexpected, intramolecular Diels-Alder reaction product **23** instead of the desired triple-layered anthracenophane, the structure of which was determined by spectral data and X-ray crystallographic analysis.[5]



22



23 (R: H,CH$_3$)



24

Interconversion between 3 and 22. Pyrolysis of **12** and the succeeding work-up in the dark produced the *anti*- and *syn*-anthracenophanes (**1** and **3**). However, the same procedure in a bright room gave an unexpected mixture of **1** and its isomer **22**. The structure of **22** was confirmed by the absence of characteristic absorption bands in the electronic spectrum, NMR data, and finally by X-ray crystal structure analysis[1,7] as shown in Fig. 1. On the basis of the above results, it is reasonable to presume that the initially formed **3** might be isomerized to **22** by irradiation with scattered day light in the room, as in the photodimerization of anthracene to anthracene dimer (trivial name, dianthracene) (**25**). Irradiation with sunlight or monochromatic light (374 nm) of a solution of pure **3** gave immediately and quantitatively the photo-isomer **22**. The reverse reaction of **25** to anthracene is known to proceed at 200—270 °C.[8] The similar reverse reaction of **22** to **3** was performed under various pyrolytic conditions as shown in Tables 1 and 2. The optimum yield of **3** was achieved by heating **22** at 198—199 °C for 6 h under nitrogen stream (Table 1). However, when the pyrolysis was performed in solution (Table 2), a mixture of **1** and **3** was obtained and the ratio of **1**: **3** increased rapidly as the reaction proceeded. The difference in the pyrolytic reaction in the solid and in the solution can be understood as follows. In the solution an anthracene ring of biradical species **24**, which is formed by the homolytic cleavage of an sp^3-sp^3 single bond of **3**, can rotate to give thermodynamically stable *anti*-isomer **1**, while in the solid state the aromatic ring is unable to rotate due to less degrees of freedom for molecular motion and therefore more hindered *syn*-isomer **3** is afforded selectively. On the other hand, a photochemical interconversion was observed between **22** and **3**. Thus, when a solution of **22** in THF was exposed to monochromatic light (254 nm) for 10 min, **3** was observed in the resulting electronic spectrum and conversely, **3** to **22** by irradiation of 374 nm light.

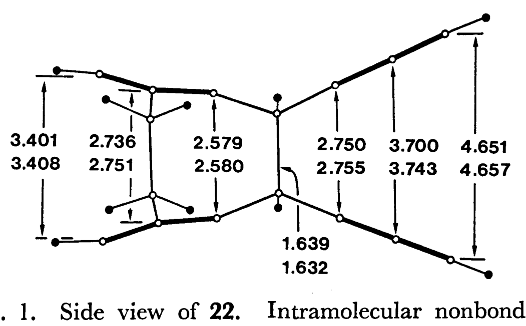
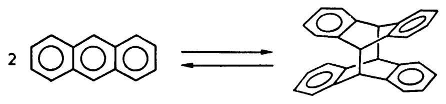


Fig. 1. Side view of **22**. Intramolecular nonbonding distances (Å) and single bond distances between bridgehead atoms are also given.



25

Table 1. Thermal isomerization of **22** to **3** in solid state

Temp (°C)	Reaction time (h)	Yield (%)	Decomposition product
196—203[a]	24	68.5	no
198—199[a]	6	quantitative	no
209—213[a]	6	69.4	exist
219—221[a]	6	23.9	exist
197—200[b]	6	83.2	trace
197—201[b]	6	85.1	trace

a) Under N$_2$. b) In sealed tube.

Table 2. Thermal isomerization of **22** to **1** and **3** in hexachlorobutadiene

	Reac. temp	199—201 °C		215—221 °C	
	Product ratio[a]	**1/22**	**3/22**	**1/22**	**3/22**
Reac. time (min)	5	0	0	0.14	0.14
	10	0	0.10	0.50	0.18
	15			0.98	0.31
	20	0.19	0.14		
	25			1.1	0.28
	30	0.43	0.20		
	45			3.8	0.30
	60	1.92	0.19		

a) Values were determined by the intensities in NMR spectra.

The molecular structure of **22** and **3**[1] were determined by X-ray analysis, in order to clarify the reason for the easier interconversion between **22** and **3** than that between anthracene dimer and anthracene and to

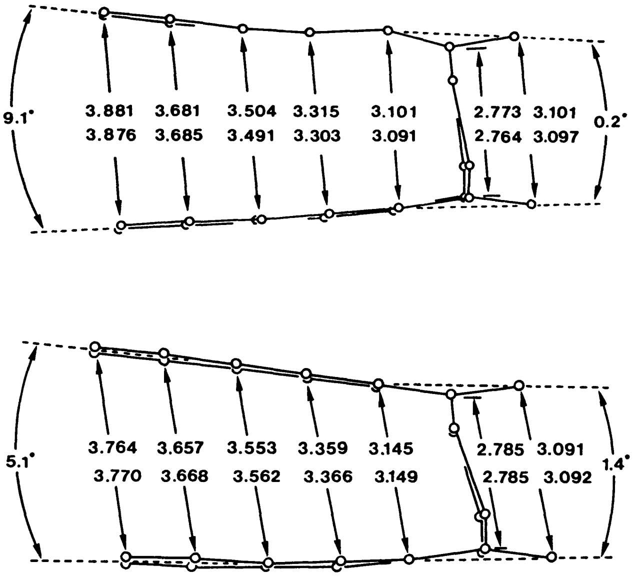


Fig. 2. Side view of the two anthracenophane molecules in crystal of **3**. Intramolecular nonbonding distances (Å) and dihedral angles are also given.

relate the structures of a series of anthracenophanes to their spectral data. Figure 1 shows marked elongation (1.632 and 1.639 Å) of the C_{sp^3}–C_{sp^3} bond in question from the normal value (1.54 Å) compared with the corresponding bond (1.61 Å) of anthracene dimer **25**,[9] indicating that there is greater strain in **22** causing easier breaking of the bond. Analysis of **3** showed two different anthracenophane molecules in each asymmetric unit of the crystal lattice. As seen in Fig. 2,[1] the non-bonding interatomic distances (3.315 and 3.303 Å) between the corresponding sp^2 carbon atoms in one of the two anthracenophane molecules are relatively shorter than the van der Waals distance, showing considerable overlap between the two $2P_z$ orbitals. In other words, it indicates easy formation of a covalent bond between the two carbon atoms. As a result the ready interconversion between **22** and **3** is understandable from the above analytical data.

NMR Spectra. NMR data of the compounds **1**—**11** are summarized in Table 3. The spectrum of *anti*-anthracenophane **1** was recorded in arsenic trichloride because of the low solubility in the usual

Table 3. NMR data of anthracenophanes (δ values in $CDCl_3$)

Compd	Aromatic proton	Calcd shift	Me
1[a]	H_c 5.47 (s)	−1.78	
	H_d 8.32 (s)	−0.24	
	H_e 8.13 (m)	+0.04	
	H_f 7.62 (m)	+0.08	
2	H_{a_1} 7.48 (A_2B_2)	−0.84	
	H_{a_2} 8.02 (A_2B_2)	−0.30	
	H_{b_1} 6.30 (A_2B_2)	−1.19	
	H_{b_2} 7.3—7.5 (m)		
	H_c 5.80 (s)	−1.39	
	H_d 7.84 (s)	−0.67	
	H_e 7.73 (A_2B_2)	−0.29	
	H_f 7.3—7.5 (m)		
3	H_c 6.71 (s)	−0.48	
	H_d 7.80 (s)	−0.71	
	H_e 7.39 (A_2B_2)	−0.63	
	H_f 6.96 (A_2B_2)	−0.52	
4	H_c 5.71 (s)	−1.48	
	H_d 8.23 (s)	−0.28	
	H_g 5.44 (s)	−1.71	
	H_e H_f H_h H_i } 7.3—8.1 (m)		
5	H_c 6.73 (s) or 6.71 (s)	−0.46 or −0.48	
	H_d 7.87 (s)	−0.64	
	H_e 7.69 (A_2B_2)	−0.33	
	H_f 7.34 (A_2B_2)	−0.14	
	H_g 6.73 (s) or 6.71 (s)	−0.42 or −0.44	
	H_h 7.25 (A_2B_2)	−0.71	
	H_i 6.30 (A_2B_2)	−1.16	
6	H_{a_1} H_{a_2} H_{b_1} } 6.8—8.2 (m)		
6	H_{b_2} H_h H_i } 6.8—8.2 (m)		
	H_g 5.81 (s)	−1.34	
7	H_c 6.69 (s)	−0.50	
	H_d 8.20 (s)	−0.31	
	H_e 7.97 (m)	−0.05	
	H_f 7.51 (m)	+0.03	
	H_{j_1} 5.29 (d)	−1.77	
	H_{j_2} 6.52 (d)	−0.54	
8	H_a 7.93 (m)	−0.39	
	H_b 7.30 (m)	−0.19	
	H_j 5.56 (s)	−1.50	
9	H_{c_1} 6.58 (AB)	−0.61	1.16 (s)
	H_{c_2} 6.90 (AB)	−0.29	2.16 (s)
	H_{d_1} 8.35 (s)	−0.16	
	H_{d_2} 8.17 (s)	−0.34	
	H_{k_1} 5.10 (s)	−1.80	
	H_{k_2} 6.14 (s)	−0.76	
	H_e 7.8—8.3 (m)		
	H_f 7.3—7.7 (m)		
10	H_{a_1} H_{a_2} } 7.7—8.3 (m)		1.56 (s)
	H_{b_1} H_{b_2} } 6.9—7.6 (m)		
	H_k 5.27 (s)	−1.63	
11	H_c 6.33 (s)	−0.86	1.81 (s)
	H_d 7.94 (s)	−0.57	1.54 (s)
	H_e H_f } 7.2—7.9		
	H_{k_1} 4.40 (s)	−2.50	
	H_{k_2} 5.70 (s)	−1.20	
	H_{k_3} } 5.54 (s)	−1.36	
	H_{k_4} } 5.51 (s)	−1.39	

a) in $AsCl_3$.

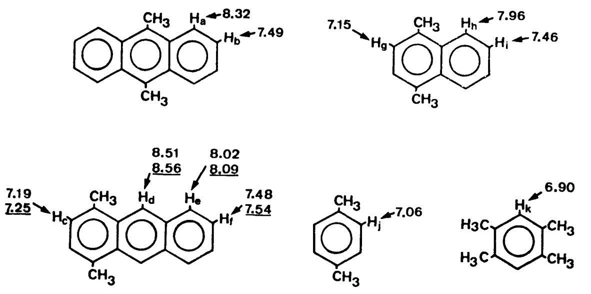


Fig. 3. NMR data of reference compounds, δ values in $CDCl_3$. Values with underline are in $AsCl_3$.

organic solvents. All the methylene proton signals appear separately as two groups of multiplets. The aromatic protons are assigned by reference to their coupling modes and the chemical shifts of non-layered compounds. The signals appear generally at higher field owing to the anisotropic effect of a faced aromatic ring or two benzene rings in the case of **11**, compared with those of the reference compounds. This effect was estimated by using the chemical shifts (Fig. 3) of the corresponding protons of 9,10- and 1,4-dimethylanthracenes, 1,4-dimethylnaphthalene, *p*-xylene, and durene as standards (Table 3). Of these values, marked upfield shifts (over 1 ppm) were observed for H_c's of **1**, **2**, and **4**, $H_{b'}$ of **2**, H_g's of **4** and **6**, H_i of **5**, $H_{j'}$ of **7**, H_j of **8**, $H_{k'}$'s of **9** and **11**, and H_k of **10**, all of which are located nearly above the center of the opposed aromatic ring. In triple-layered compound **11**, aromatic protons ($H_{k'}$, $H_{k''}$) of durene moiety absorb at higher field than the corresponding protons of double-layered compound **9** owing to the shielding effect of an additional benzene ring. *syn*- and *anti*-isomers [(**1** and **3**) and (**4** and **5**)] are easily distinguished by comparing the chemical shifts of H_c protons. Thus, H_c protons of the *anti*-forms (**1** and **4**) show high field shifts over 1 ppm, whereas those of the *syn*-forms (**3** and **5**) show only small high field shifts (0.48 ppm for **3**, 0.47 ppm for **5**). A slight down field shift was observed for H_e and H_f of **1** and H_f of **7**. These protons are situated far apart from the center of the opposite ring and hence, it is assumed that they are in the deshielding field of the transannular ring.

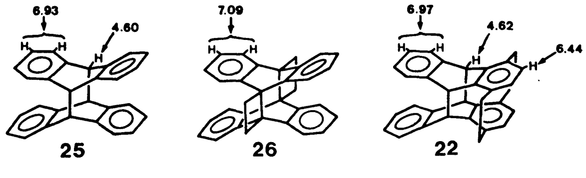


Fig. 4. NMR data of **22**, **25**, and **26** in $AsCl_3$.

NMR data of photo-adduct **22** are also shown in Fig. 4 together with those of two related compounds **25** and **26**. The chemical shifts of the corresponding protons reflect the similar molecular structure among the three compounds, *i.e.*, **22** (Fig. 1),[7] **25**,[9] and **26**.[10]

Electronic Spectra. The electronic spectra of anthracenophanes **1**—**11** are shown in Figs. 5—8 together with those of the reference compounds. Characteristic features of these spectra are eminent broadening of and considerable bathochromic and hypochromic shifts of ^1L_a band of anthracene chromophore compared with those of acyclic compounds, indicating obvious transannular π-electronic interaction. It may be easily understood from Fig. 6 that the magnitude of the transannular interaction is associated with the extent of overlap of the two chromophores. Thus, the longest wavelength bands of fully overlapped isomers **5** and **6** show large bathochromic shifts, while the spectrum of the least overlapped isomer **4** moderately resembles that of the reference compound. The same features are seen in Fig. 5. Anthracenophanes **2** and **3**, where two anthracene rings are stacked fully or appreciably, absorb in longer wavelength region than *anti*-isomer **1**.

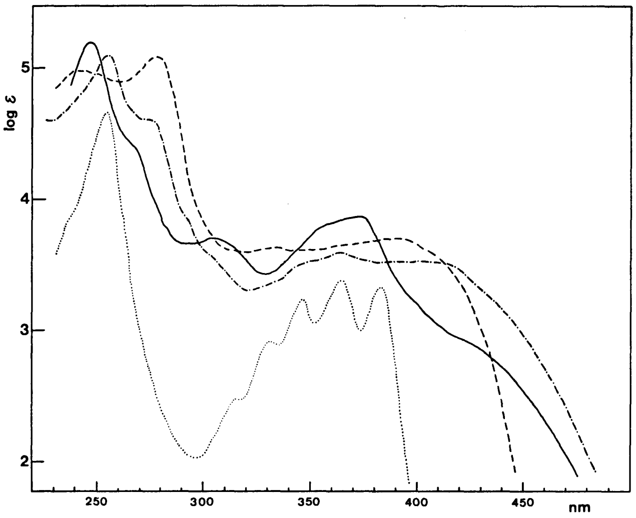


Fig. 5. Electronic spectra of **1** (——), **2** (-·-·-), **3** (——), and 1,4-dimethylanthracene (······) in tetrahydrofuran. The curve of 1,4-dimethylanthracene is displaced downward by 0.5 log ε unit.

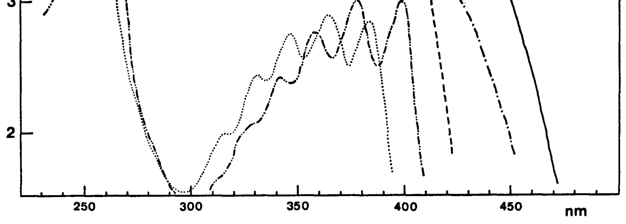


Fig. 6. Electronic spectra of **4** (——), **5** (-·-·-), **6** (——), 1,4-dimethylanthracene (······), and 9,10-dimethylanthracene (-··-) in tetrahydrofuran. The curves of two dimethylanthracenes are displaced downward by a log ε unit.

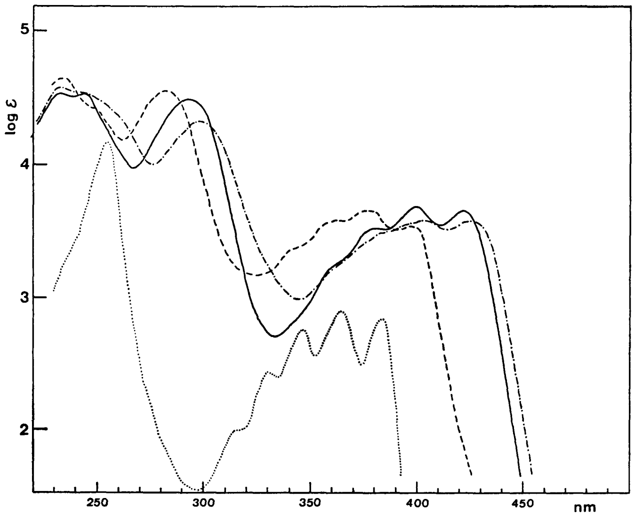


Fig. 7. Electronic spectra of **7** (-----), **8** (——), **10** (-•--•-), and 1,4-dimethylanthracene (······) in tetrahydrofuran. The curve of 1,4-dimethylanthracene is displaced downward by a log ε unit.

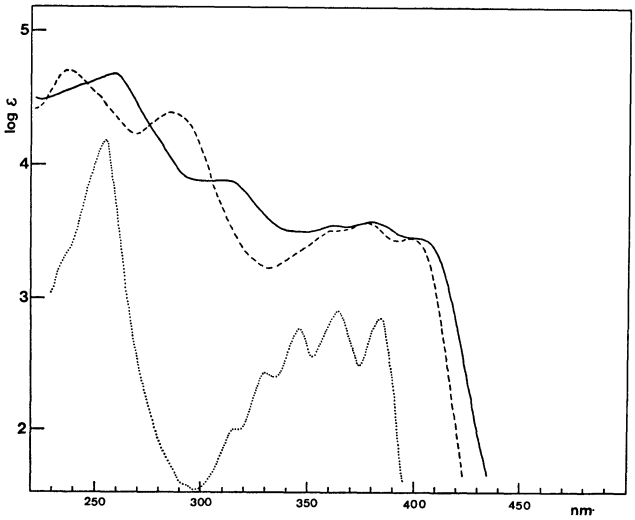
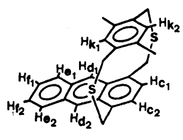


Fig. 8. Electronic spectra of **9** (-----), **11** (——), and 1,4-dimethylanthracene (······) in tetrahydrofuran. The curve of 1,4-dimethylanthracene is displaced downward by a log ε unit.

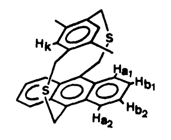
Let us consider an alternate groups of anthracenophanes, *i.e.*, compounds **1**, **4**, and **7**, which have the same degree of overlapping between the two faced rings and therefore probably the same degree of molecular strain. Of these three compounds, only **1** shows a structureless band in the region of 320—450 nm, indicative of extensive transannular interaction. The magnitude of the red shift of this band is largest for **1** and smallest for **7** compared with the reference compound. In other words, this implies that the transannular interaction increases in the order of **1**>**4**>**7**, that is, in the order of dimension of the faced chromophore. The same tendency is seen by comparing the spectrum of **2** with those of **5** and **6**. These observations may be interpreted by means of the exciton type interaction, which predicts that the smaller the difference in the transition energies of composite chromophores, the greater the configuration interaction between them; that is to say, the interaction is the strongest when the chromophores under consideration are the same. Theoretical treatment[11] of double-, triple-, and quadruple-layered cyclophanes has shown that their transannular bands in the longest wavelength region originate from the exciton interaction of composite chromophores with some degree of charge transfer character. Thus, it seems reasonable to assume the existence of similar excition interaction in anthracenophanes as above stated.

Triple-layered compound **11** absorbs at somewhat longer wavelength than double-layered one **9** (Fig. 8), indicating the increase of the transannular effect.

The fluorescence spectra of three isomeric anthracenophanes **1**—**3** are of particular interest in relation to the geometrical structure of excimers. This study has been reported in a separated paper.[12]



27



28

Experimental

All melting points are uncorrected. The NMR spectra were recorded on a Hitachi Perkin-Elmer R-20 or on a Varian XL-100. The UV and MS spectra were measured with a Hitachi EPS-3T and a Hitachi RMU-7, respectively.

Ethyl 4-Methylanthracene-1-carboxylate (18). Esterification of 4-methylanthracene-1-carboxylic acid (**17**)[13] was performed in the usual manner. **18**: yellow columns from petro-

Table 4. Analytical data, recrystallization solvents, and yields of anthracenophanes

Compound	Formula	Calcd %		Found %		Mp (°C)	Recryst solvent
		C	H	C	H		
2	$C_{32}H_{24}$	94.08	5.92	93.89	5.70	262.0—264.0	benzene
4	$C_{28}H_{22}$	93.81	6.19	93.70	5.91	246.5—247.5	toluene
5	$C_{28}H_{22}$	93.81	6.19	93.65	6.01	221.0—222.0	benzene–hexane (1:9)
6	$C_{28}H_{22}$	93.81	6.19	93.99	6.05	230.5—231.5	benzene
7	$C_{24}H_{20}$	93.46	6.54	93.23	6.41	172.0—173.5	benzene–hexane (1:9)
8	$C_{24}H_{20}$	93.46	6.54	93.51	6.40	168.5—173.0	benzene
11	$C_{36}H_{34}$	92.66	7.34	92.44	7.21	217.0—218.5	benzene–hexane (1:1)

leum ether, mp 66.0—66.5 °C.

Found: C, 81.67; H, 5.99%. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10%.

4-Methyl-1-(bromomethyl)anthracene (20). To a stirred suspension of $LiAlH_4$ (7.83 g) in dry ether (300 ml) was added dropwise a solution of **18** (74.8 g, 0.283 mol) in the same solvent (650 ml). After the addition was over, the mixture was stirred under reflux for 5 h, then at room temperature for 12 h. Water and 6 M aq HCl were successively added to the reaction mixture which was then extracted with ether and the organic layer was worked-up in the usual manner. Removal of the solvent gave yellow crystals (60.8 g, 96.8%) of **19**, which were used for the following reaction without further purification. To a stirred suspension of **19** (60.8 g, 0.274 mol) in CCl_4 (1 liter) was added a solution of PBr_3 (14 ml) in CCl_4 (200 ml). After the addition was over, the reaction mixture was heated at 50—53 °C for 10 h. Water (150 ml) was added and the mixture was extracted with CCl_4. The organic layer was worked-up in the usual manner and after recrystallization from CCl_4, pure **20** was obtained as yellow columns, 73.4% yield, mp 132.5—133.5 °C.

Found: C, 67.05; H, 4.34; Br, 27.79%. Calcd for $C_{16}H_{13}Br$: C, 67.38; H, 4.59; Br, 28.02%.

(4-Methyl-1-anthrylmethyl)trimethylammonium Bromide (21). An excess of trimethylamine (40 g) in ether was added with stirring to a cooled solution of **20** (49.2 g, 0.173 mol) in ether (5 l). After prolonged stirring, the resulting ppt was filtered, washed with ether, and dried. The yield of quaternary ammonium bromide **21** was 58.5 g (98.5%).

*Synthesis of **1**—**8** and **11** by the Hofmann Elimination Reaction.* All the coupling reactions of ammonium salts were undertaken according to the general procedure, which is described in detail for the case of (4-methyl-1-anthrylmethyl)trimethylammonium bromide **21** as follows.

An aq solution of **21** was passed through a column of anion exchange resin (Dowex 1-X8) to give an aq solution of ammonium base **12**. The soln thus obtained was added dropwise to a boiling solution of phenothiazine in xylene (0.2 g per 3 l of xylene) which was placed in a three-necked flask equipped with a condenser, mechanical stirrer, and water separator. After water separation was over, additional heating was continued for 24 h. The insoluble solid was filtered off and the filtrate dried over $MgSO_4$. The solvent was removed *in vacuo* until a small amount of the solvent was left. By this treatment *anti*-[2.2](1,4)anthracenophane **1** was precipitated from the solution. An additional amount of the compound **1** was obtained by benzene extraction of the insoluble solid above described. The total yield of **1** was about 60%. Recrystallization from xylene gave pure **1** as colorless prisms, dec over 300 °C.

Found: C, 93.95; H, 5.78%; M^+, 408. Calcd for $C_{32}H_{24}$: C, 94.08; H, 5.92%; M, 408.51.

The mother liquor was chromatographed on Al_2O_3 (Woelm, Activity I) to give **22** (1.9% yield). Recrystallization from AcOEt–EtOH gave pure **22** as colorless prisms, mp 242—243 °C with dec.

Found: C, 94.23; H, 5.82%; M^+, 408. Calcd for $C_{32}H_{24}$: C, 94.08; H, 5.92%; M, 408.51.

When the above reaction was carried out in the dark, **3** was obtained after filtration of the reaction mixture and evaporation of the solvent. Crude **3** was purified from the *anti*-isomer by the following manner. First it was recrystallized from benzene to give **3** containing 5% of **1**. Then, the crystals were dissolved in a minimum amount of benzene, the solution was frozen in a deep-freezer, and warmed up to room temperature. After most of the solid was dissolved, it was filtered as soon as possible to remove less soluble *anti*-isomer **1**. The above procedure was repeated once or twice and recrystallization from CCl_4 gave pure **3** as yellow plates, 250 °C dec.

Found: C, 93.91; H, 5.76%; M^+, 408. Calcd for $C_{32}H_{24}$: C, 94.08; H, 5.92%; M, 408.51.

Elemental analyses, melting points, recrystallization solvents, and yields of the other anthracenophanes are summarized in Table 4.

5,8-Dimethyl-2,11-dithia[3.3]paracyclo(1,4)anthracenophane (27). A solution of 1,4-bis(bromomethyl)anthracene[14] (1.82 g, 5.0 mmol) in benzene (300 ml) and a solution of 1,4-dimethyl-2,5-bis(mercaptomethyl)benzene[6] (0.99 g, 5.0 mmol) and sodium hydroxide (0.4 g) in 95% ethanol (50 ml) were added dropwise and simultaneously through dropping funnels into boiling ethanol (150 ml) over a period of 5 h under N_2 with vigorous stirring. After further heating and stirring for 18 h, the solvents were evaporated off and the residue was extracted with benzene. The benzene solution was passed through a short column of silica gel to yield a yellow solid. This was recrystallized from benzene to give pure dithiacyclophane **27** (1.09 g, 54.5%) as yellow prisms, dec>236 °C in a sealed tube.

Found: C, 78.06; H, 5.80; S, 15.92%; M^+, 400. Calcd for $C_{26}H_{24}S_2$: C, 77.95; H, 6.04; S, 16.01%; M, 400.58. NMR ($CDCl_3$, δ): 1.18 (s, 3, *endo*-Me), 2.38 (s, 3, *exo*-Me), 4.64—3.50 (m, 8, CH_2), 6.16 (s, 1, H_{k1}), 6.73 (s, 1, H_{k2}), 6.74 (AB, J=8 Hz, 1, H_{c1}), 7.04 (AB, J=8 Hz, 1, H_{c2}), 7.0—7.8 (m, 2, H_{f1} and H_{f2}), 7.8—8.4 (m, 2, H_{e1} and H_{e2}), 8.53 (s, 1, H_{d2}), 8.73 ppm (s, 1, H_{d1}).

4,7-Dimethyl[2.2]paracyclo(1,4)anthracenophane (9). A solution of dithiacyclophane **27** (2.0 g, 5.0 mmol) in benzene (400 ml) and triethyl phosphite (500 ml) was irradiated internally with a high pressure mercury lamp (400 W) for 9 h whilst a slow stream of N_2 was bubbled through. After removal of the solvents, the resulting solid was chromatographed on silica gel with benzene to yield the desired cyclophane **9** (1.24 g, 73.7%), yellow prisms from benzene, mp 235.0—235.5 °C with dec in a sealed tube.

Found: C, 92.59; H, 6.98%; M^+, 336. Calcd for $C_{26}H_{24}$: C, 92.81; H, 7.19%; M, 336.45.

5,8-Dimethyl-2,11-dithia[3.3]paracyclo(9,10)anthracenophane (28). A solution of 9,10-bis(chloromethyl)anthracene[15] (3.3 g, 12.0 mmol) in benzene (500 ml) and a solution of 2,5-bis(mercaptomethyl)-*p*-xylene (2.38 g, 12.0 mmol) and sodium hydroxide (1.0 g) in 90% ethanol were added dropwise and simultaneously through dropping funnels into boiling ethanol (200 ml) for 3.75 h under N_2. The mixture was refluxed for an additional 12 h and worked up in the same manner as in the synthesis of **27** to afford 3.06 g (63.7%) of **28**. It was recrystallized from benzene to give a yellow powder, dec>230 °C in a sealed tube.

Found: C, 77.94; H, 5.96; S, 15.79%; M^+, 400. Calcd for $C_{26}H_{24}S_2$: C, 77.95; H, 6.04; S, 16.01%; M, 400.58. NMR ($CDCl_3$, δ): 1.51 (s, 6, Me), 3.58 (AB, J=15 Hz, 2, CH_2 attached to durene moiety), 3.85 (AB, J=15 Hz, 2, CH_2 attached to durene moiety), 4.89 (bs, 4, CH_2 attached to anthracene moiety), 6.20 (s, 2, H_k), 7.3—7.8 (m, 4, H_{b1} and H_{b2}), 8.1—8.6 ppm (m, 4, H_{a1} and H_{a2}).

4,7-Dimethyl[2.2]paracyclo(9,10)anthracenophane (10). In the same manner as **9**, irradiation of a solution of disulfide **28** (4.0 g, 10 mmol) in 1 liter of benzene and triethyl phosphite (1:1) for about 5 h and purification by column chromatography on silica gel gave the cyclophane **10** (1.99 g, 59.2%), yellow needles from dichloromethane–petroleum ether, dec> 170 °C in a sealed tube.

Found: C, 92.15; H, 6.94%; M^+, 336. Calcd for $C_{26}H_{24}$: C, 92.81; H, 7.19%; M, 336.45.

We are greatly indebted to Mr. T. Fujino for microanalyses and to Mr. Y. Takai for NMR measurements. The present work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education.

References

1) Part LI: T. Toyoda and S. Misumi, *Tetrahedron Lett.*, **1978**, 1479.

2) S. Misumi, *Mem. Inst. Sci. and Ind. Res., Osaka Univ.*, **33**, 53 (1976); S. Misumi and T. Otsubo, *Acc. Chem. Res.*, **11**, 251 (1978).

3) a) W. Baker, F. Glockling, and J. F. W. McOmie, *J. Chem. Soc.*, **1951**, 1118; b) W. Baker, J. F. W. McOmie, and W. K. Warburton, *ibid.*, **1952**, 2991; c) D. J. Cram, C. K. Dalton, and G. R. Knox, *J. Am. Chem. Soc.*, **85**, 1088 (1963); d) G. W. Brown and F. Sondheimer, *ibid.*, **89**, 7116 (1967); e) H. J. Reich and D. J. Cram, *ibid.*, **91**, 3527 (1969); f) J. M. McBride, P. M. Keehn, and H. H. Wasserman, *Tetrahedron Lett.*, **1969**, 4147; g) H. H. Wasserman and P. M. Keehn, *J. Am. Chem. Soc.*, **91**, 2374 (1969); h) M. Haenel and H. A. Staab, *Tetrahedron Lett.*, **1970**, 3585; i) M. Haenel and H. A. Staab, *Chem. Ber.*, **106**, 2203 (1973); j) M. W. Haenel, *Tetrahedron Lett.*, **1974**, 3053; k) J. R. Davy and J. A. Reiss, *Aust. J. Chem.*, **29**, 163 (1976).

4) J. H. Golden, *J. Chem. Soc.*, **1961**, 3741.

5) T. Toyoda, A. Iwama, T. Otsubo, and S. Misumi, *Bull. Chem. Soc. Jpn.*, **49**, 3300 (1976).

6) F. Imashiro, M. Oda, T. Iida, Z. Yoshida, and I. Tabushi, *Tetrahedron Lett.*, **1976**, 371.

7) T. Toyoda, Dissertation, Osaka University, Osaka, 1976.

8) D. E. Applequist, R. L. Litle, E. C. Friedrich, and R. E. Wall, *J. Am. Chem. Soc.*, **81**, 452 (1959).

9) M. Ehrenberg, *Acta Crystallogr.*, **20**, 177 (1966).

10) M. Ehrenberg, *Acta Crystallogr.*, **20**, 182 (1966).

11) S. Iwata, K. Fuke, M. Sasaki, S. Nagakura, T. Otsubo, and S. Misumi, *J. Mol. Spectrosc.*, **46**, 1 (1973).

12) T. Hayashi, N. Mataga, Y. Sakata, S. Misumi, M. Morita, and J. Tanaka, *J. Am. Chem. Soc.*, **98**, 5910 (1976); M. Morita, T. Kishi, M. Tanaka, J. Tanaka, J. Ferguson, Y. Sakata, S. Misumi, T. Hayashi, and N. Mataga, *Bull. Chem. Soc. Jpn.*, in press.

13) R. Scholl, A. Keller, K. Meyer, and H. Penz, *Justus Liebigs Ann. Chem.*, **512**, 30 (1934).

14) K.-D. Gundermann and K.-D. Röker, *Justus Liebigs Ann. Chem.*, **1976**, 140.

15) M. W. Miller, R. W. Amidon, and P. O. Tawney, *J. Am. Chem. Soc.*, **77**, 2845 (1955).